Short communication

A new method for detecting lithium plating by measuring the cell thickness

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HIGHLIGHTS

- A new method for the detection of lithium plating is described.
- The measurement shows a reversible and an irreversible part of lithium plating.
- Fast mapping of the maximum current at different temperatures is possible.

ABSTRACT

Charging Li-ion cells at low temperatures and/or high currents can cause the lithium ions to deposit on the anode surface rather than intercalating into the graphite lattice. This effect, named lithium plating, may severely affect the performance, reliability and safety of the cell. Because metallic lithium at the anode consumes more space than intercalated into the graphite, the cell volume increases in the case of lithium plating. An experimental setup for precise measuring the thickness of pouch cells with a resolution of 1 μm was built. The cell thickness as a function of its charge under standard cycling conditions was recorded as a reference. In the case of lithium plating an additional increase of the thickness was observed. This can be used as an indicator for the non-destructive detection of lithium plating in pouch cells. Compared with the standard capacity based methods this procedure allows a higher sensitivity and gives results more quickly.

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1. Introduction

Due to the wide range of environmental influences Li-ion batteries in automotive applications have to meet high standards. Besides mechanical stability and safety in crash scenarios the wide range of operating temperature poses a great challenge. Particularly acceptable charge rates combined with low temperatures is still a major challenge.

At temperatures below 10 °C charging Li-ion cells with standard graphite based anodes, the currently most common used anode material, is only possible at a fraction of the nominal charge rate. The limiting factor is the intercalation speed of the lithium ions into the anode, which is significantly decreasing at lower temperatures. Exceeding a specific charge current, this leads to the damaging effect of lithium plating, i.e., the deposition of metallic lithium at the anode.

The effect has a negative impact on performance, reliability and safety of the cell. The deposited lithium is not available anymore for the ionic charge transfer which results in a loss of capacity. In addition the metallic lithium reacts with the electrolyte increasing the solid electrolyte interface (SEI), which causes a rise of the internal resistance.

Besides the electrical parameters, the safety aspect of lithium plating has to be considered. The deposition of lithium on the anode is not uniform, but rather in form of dendrites which can grow through the separator. This can lead at least theoretically to soft shorts resulting in higher self discharge or to a short circuit causing a thermal runaway. To guarantee safety, performance and long life an operation condition causing lithium plating has to be avoided by all means.

2. Theory

2.1. Lithium plating

Under normal circumstances Li-ion batteries do not contain metallic lithium at all. Only Li-ions are moving through the

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electrolyte and intercalate into the anode during charge and vice versa into the cathode during discharge. Under certain operating conditions, particularly while charging at low temperature and/or with high currents, lithium ions deposit at the anode surface rather than intercalating into the graphite lattice [1]. This can only occur if the anode potential drops below the potential of 0 V vs. Li/Li$^+$. Depending on the temperature and charge current this can occur any time after starting the charge process or when overcharging the cell [2].

During plating there persists a coexistence between the intercalation of the ions into the lattice and deposition on the surface of the anode. This state remains, until the charge process is stopped or the current in the constant voltage mode is small enough so that the anode potential can recover to a potential above Li/Li$^+$ [3].

A large part of the lithium deposition is reversible [1,2,4,5,15]. Thereby the reduction of plated lithium can take place either through subsequent chemical intercalation into the graphite lattice, which needs sufficient relaxation time, or by dissolving during the following discharge. In the latter case lithium is oxidizing at a potential which is about 100 mV more negative than the deintercalation potential of lithium in graphite [1], resulting in a higher voltage while discharging at low current. This characteristically higher voltage plateau at the discharge voltage graph gives evidence of lithium plating [1]. Since the plateau indicates the reversible part of plating only, a quantitative measurement of the total amount of deposited lithium is not provided.

2.2. Characterization of lithium plating behavior

State of the art methods for detecting lithium plating can be categorized in three types, depending on the effect they rely on:

(i) Detecting a negative anode potential vs. Li/Li$^+$, e.g., with a reference electrode or in half cells.
(ii) Electrical measurement of the cell degradation through plating e.g., loss of capacity, rise of internal resistance.
(iii) Physical/chemical post mortem analysis and proof of metallic lithium.

By now, the only way of detecting lithium plating in progress is method (i), that is measuring the anode potential, either in half cells or through a built-in reference electrode. Both methods need massive modification of a given cell. Moreover, a reference electrode may interfere with the electrode processes and has a negative influence on the measurement [4,14].

For the characterization of unmodified cells in large-scale production measuring the anode potential is not an option. The standard procedure of determining the onset of plating is mapping the maximum charge current at different operating conditions, while periodically checking the performance degradation (ii). The most important parameter here is the degradation of the cell's capacity, since it correlates directly with the loss of active lithium.

Besides the non-invasive electrical tests, a further post mortem analysis (iii) can provide a better picture of the nature of the cell degradation. The wide range of chemical and physical analysis methods will not be addressed here.

2.3. Volume change during cycling

It is well known that active materials vary in volume, depending on the amount of intercalated Li-ions. Graphite anodes, for example, gain about 10% in volume while changing from the unlithiated elementary state to fully lithiated LiC$_6$ [6]. As the common cathode materials have a much smaller dilatation coefficient, e.g., NMC: about 1% [7], the thickness of graphite based batteries is

governed by the anode volume change. On the other hand lithium titanate anodes (LTO) for instance are almost unaffected by the amount of intercalated lithium, since its volume change is only 0.1%–0.3% [8].

2.4. Volume change through lithium plating

Lithium can fill the free interstitials when intercalated into the graphite lattice. Hence, the volume of the intercalation compound is smaller than the volume of the two separate materials. While the deintercalation from the cathode has no significant effect on the cell thickness, depositing lithium on the surface instead of intercalating into the anode leads to an additional gain in the overall volume.

The following example estimates the expected extent of volume gain by lithium plating. Side effects like change in porosity, gas evolution, dendritic growth or inhomogeneity within the cell are neglected in the following calculation.

Transferring 1 Ah of charge from the cathode to the anode, the amount of lithium substance is:

$$n_{Li}(1 \text{ Ah}) = \frac{C}{e \cdot N_A} = 37.31 \text{ mmol} \tag{1}$$

n_{Li}: amount of Li substance [mol], N_A: Avogadro constant [1/mol], e: elementary charge [As]; C: transferred charge [As].

Fully charged, every six carbon atoms provide space for one lithium atom. Thus for 1 Ah of charge an amount of $6 \cdot n_{Li} = 223.9 \times 10^{-3}$ mol of carbon is consumed. With the molar volume of carbon in hexagonal structure of 5.31×10^{-6} m^3 mol^{-1} its volume is 1.189 cm^3. According to the literature, carbon based anode materials expand about 10% due to the intercalation of lithium [6]. Thereby charging 1 Ah causes a volume change of:

$$\Delta V_C(1 \text{ Ah}) = \alpha_{LiC_6} \cdot n_{Li}(1 \text{ Ah}) \cdot 6 \cdot V_{m,C} = 0.12 \text{ cm}^3 \tag{2}$$

ΔV_C: Change of the carbon volume due to lithium intercalation [m^3], α_{LiC_6}: coefficient of expansion changing from C to LiC$_6 \approx 10\%$, $V_{m,C}$: molar volume of carbon [m^3 mol^{-1}].

With a molar volume of $V_{m,Li} = 13.02 \times 10^{-6}$ m^3 mol^{-1} the volume of lithium in metallic condition providing 1 Ah of charge is 0.49 cm^3.

If the lithium is depositing rather than intercalating, the resulting expansion equals the volume of the lithium in metallic form minus the volume the anode would gain due to the intercalation, as shown in Equation (2).

The cathode effect is neglected here. The theoretical relation between volume gain and lithium plating is therefore:

$$V_{exp}\left(C_{pl}\right) = \frac{C_{pl}}{e \cdot N_A}\left(V_{m, Li} - \alpha_{LiC_6} \cdot 6 \cdot V_{m,C}\right) \tag{3}$$

$V_{m,Li}$: molar volume of lithium [m^3 mol^{-1}], $V_{m,C}$: molar volume of carbon [m^3 mol^{-1}]; C_{pl}: amount of plated lithium.

According to Equation (3), an amount of 1 Ah of plated lithium causes a gain in volume of V_{exp} (1 Ah)= 0.37 cm^3.

The test cells used in the following experiments contain electrodes with an active area of 188 mm by 122 mm. Plating would thereby lead to a growth in thickness by 16.1 μm per plated Ah, which is independent of the amount of layers inside the cell. Note that due to the overlap, the cathode is sized smaller than the anode. Because of cell inhomogeneity, dendritic deposition and gas evolution, the actual measured value is expected to be larger.

Measuring the volume change as a method for cell characterization has already been described in the literature [6,5,9,10,12,13].

The main aspects being addressed in those works is the generated mechanical stress caused by the expansion and the corresponding aging effects. To the authors' knowledge using the cell thickness as an indicator for lithium plating has not been investigated yet.

3. Experimental

3.1. The measuring setup

A proprietary experimental setup as displayed in Fig. 1 was used to determine the change of thickness. The pouch cell is mounted between two aluminum plates, screwed together at a fixed distance. Between the upper plate and the cell an air gap is left to give room for the expansion. The mechanical and thermal connection to the bottom plate is provided by a heat conducting adhesive. This excludes measurement errors through cell slipping and provides a good thermal junction. The temperature of the bottom plate is kept constant. Moreover the whole setup is placed in a climate chamber.

One or more dial indicators can be mounted on different positions on the upper plate. The indicators used for the experiments have a resolution of 1 μm. The cycling and data acquisition is done by a BaSyTec XCPS-System in standard configuration.

3.2. Change of cell thickness under standard cycling conditions

The experiments start with the recording of a reference correlation between cell thickness and the state of charge (SOC). The method is analogous to measuring an OCV curve (open circuit voltage): The cell voltage at different SOC levels is recorded after a sufficient rest time, which allows the cell to reach an equilibrium. Monitoring the cell thickness instead of its voltage with the same procedure leads to a characteristic plot which is called open circuit thickness (OCT) in the following (Fig. 2).

The cell used for the experiments described in this paper is a high energy pouch cell with a nominal capacity of 20 Ah. The anode is graphite and the cathode is NMC based. Unless otherwise noted, this cell has been used for all experiments described in this paper. Moreover, prior to the experiments, all cells were cycled 8 times at 25° with a low current to exclude any residual formation processes.

For determining the OCT at 25 °C, the cell was charged and discharged with 5 A = $C/4$ in 1 Ah steps. After a relaxation time of 1 h at each point the measured thickness value remained stable. The resulting change of cell thickness as a function of charge is shown in Fig. 2.

Three different stages can be distinguished, each covering about a third of the total capacity, see Fig. 2. Stage I has the highest slope with about 9.5 μm Ah^{-1}. Range II has 3.0 μm Ah^{-1} and range III about 6.5 μm Ah^{-1}. The characteristic behavior is probably due to the various intercalation steps described in Ref. [11]. The same is
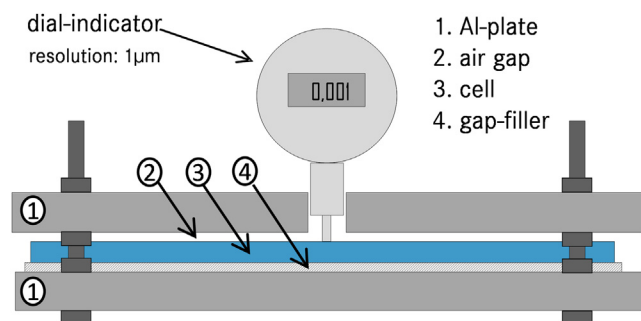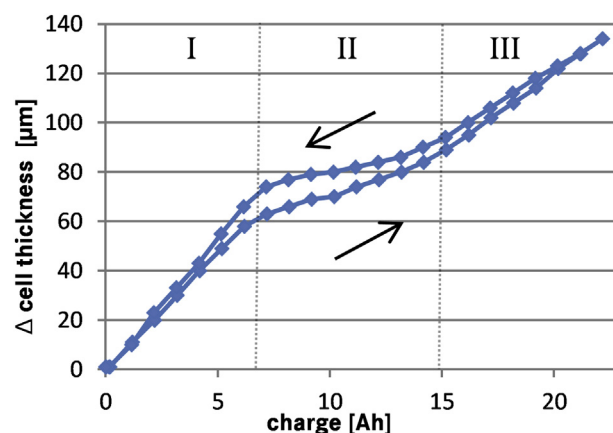

Fig. 2. OCT – cell thickness as a function of the SOC.

true for the hysteresis observed in range II. The total thickness increase of 136 μm from 0% to 100% SOC is in the range of the theoretical thickness gain of 115,9 μm for 22.158 Ah, see Equation (2). Note that in this experiment the thickness is measured in the center of the cell.

As shown in Fig. 3, charging the cell with continuous currents leads to different curves. Because there is too little time for relaxation, the three ranges of Fig. 2 become more and more indistinct with higher charge currents. Note that setup, cell type and temperature are the same as in the experiment displayed in Fig. 2. Moreover, the starting and end points of the curves differ by a few microns only. Generally, at small currents below the onset of plating the measurement shows a high grade of reproducibility.

3.3. Cathode influence

The change of cell thickness of graphite based cells is mostly due to the anode. To get an estimate of the cathode influence, an OCT of an LTO cell was measured. According to the literature [8], the LTO structure has an expansion coefficient of about 0.1%–0.3% which means it is at least three times smaller than the coefficient of NMC [04] and more than thirty times smaller than the coefficient of graphite. The OCT is therefore largely affected by the cathode expansion. The measured OCT curve of an LTO pouch cell with nominal 16 Ah is displayed in Fig. 4.

The OCT shows a difference of 6 μm between the fully charged and discharged state. Moreover, the swing of the s-shaped curve, which

Fig. 1. Setup for measuring the cell thickness with a dial indicator providing a resolution of 1 μm.
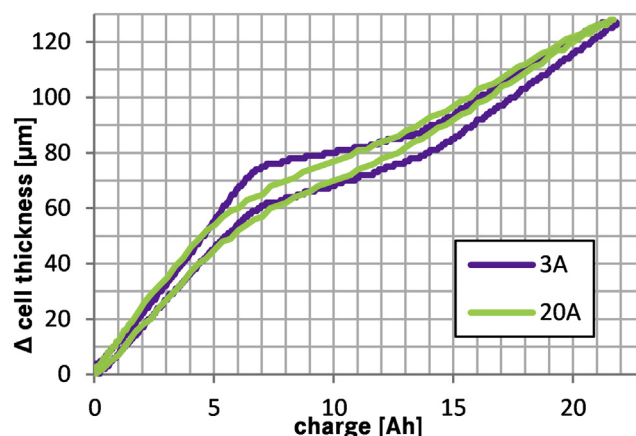

Fig. 3. Change of cell thickness during cycling with different currents at 25 °C.

also indicates the maximum cathode effect on the cell thickness, is not exceeding −9 μm/+3 μm referring to the fully charged state. In Relation to the 140 μm of expansion in a comparable graphite based cell, the cathode effect is small and was neglected in this paper.

3.4. Thermal expansion through self-heating

To exclude measurement errors through thermal expansion the effect of self-heating on the cell thickness has been investigated. Therefore the cell was heated using subsequent short charge and discharge pulses in order not to change the SOC. Note that increasing the temperature of the whole experiment would lead to additional errors due to the thermal expansion of the measuring setup.

At a temperature increase of 1 K at the cell surface the thermal expansion is smaller than the resolution of the dial indicator. Since the cell temperature was kept in a range of ±0.5 K, errors due to self-heating can be neglected.

3.5. Measuring point

Due to an existing inhomogeneity within every cell, the position of the measurement point plays a crucial role. Many pouch cells are known to start plating in a narrow area next to the cell's margin. When choosing the wrong measurement point, the experiment could therefore fail to detect the onset of lithium plating. The best point is always cell specific and has to be determined prior to the thickness measurements, e.g., by opening the cell. Fig. 5 shows a picture of the anode and cathode from the test cell after 8 cycles at 10 A and 3 cycles at 12 A at −5°. All anode layers showed severe and almost uniform plating.

3.6. Gas evolution

Side reactions as decomposition of the electrolyte or building up new SEI layers on particle cracks caused by cycling lead to the evolution of gas within the cell. Especially in pouch cells this will directly result in an increase of the measured cell thickness. To evaluate the effect two dial-indicators were mounted next to each other at a distance of 3 cm in the center area of the cell, see Fig. 6. At one dial-indicator we placed a spring which induced a pressure of about 2 bar at an area of 1.5 cm² around the measuring point increasing the pressure between the electrode layers well above the value of the surrounding area. If there was an evolution of gas, the gauge without the spring would show a significantly bigger increase of cell thickness than the one without. Fig. 7 shows a
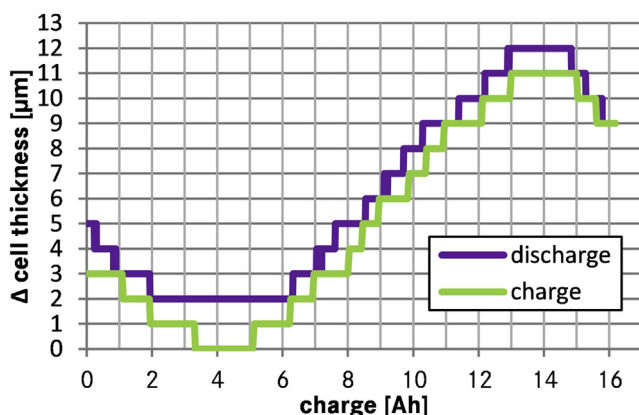

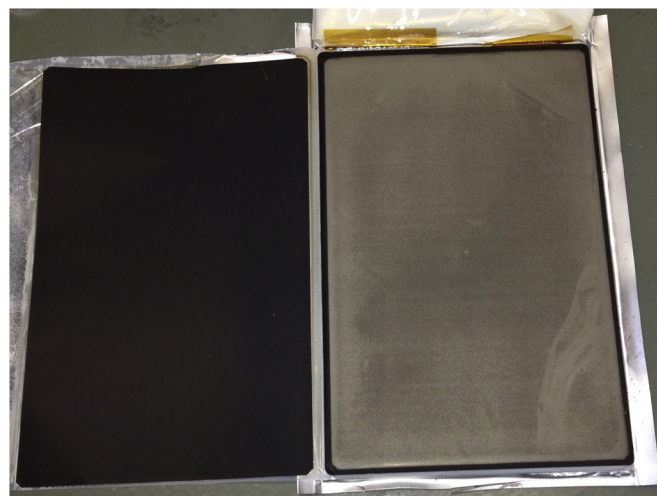**Fig. 5.** Photo of a plated anode (right) and cathode (left).

measurement at −5 °C with 3 cycles at 2.5 A and 4 cycles at 4.5 A which is just below the onset of plating at that temperature. At the end of the thickness measurement, there was no difference between the two indicators. The same is true for all similar experiments without plating where no relevant difference between the two gauges could be seen. Therefore, there seems to be no gas evolution at low temperature and at a limited number of standard cycles.

However, in the case of lithium plating, a significant difference between the two dial indicators was detected. Fig. 8 displays the change in thickness during three cycles with strong lithium plating. The setup was the same as in Fig. 7, but with a charging current of 14 A. Both curves show the typical plating characteristics as described in the following Section 3.7. However, the one without the spring has a much stronger residual increase, probably due to the evolution of gas. Independent of the exact mechanism there is an amplification of the expected thickness increase predicted by Equation (3).

3.7. Change of cell thickness during lithium plating

When charging at low temperature and low current, variation of cell thickness is quite similar to the behavior at room temperature, even though the total span decreases due to the smaller amount of usable capacity. Charging at higher currents at low temperature leads to a cell thickness behavior being different from Fig. 3. Exceeding a specific maximum charging current, an additional
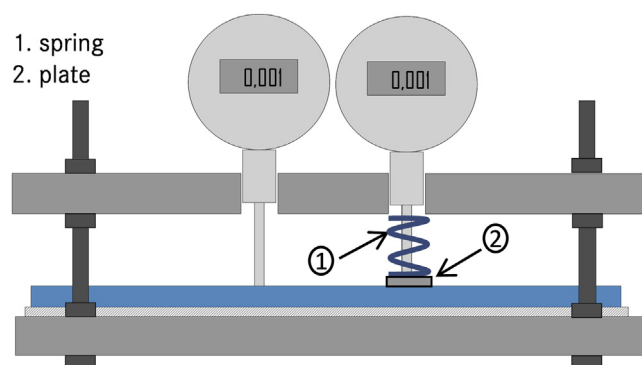

Fig. 4. Change of cell thickness at 25 °C, 16 Ah LTO pouch cell.

Fig. 6. Setup for the detection of gas evolution.

Fig. 7. Recorded cell thickness and charge during low current cycling.

Fig. 9. Change in cell thickness with and without lithium plating during one charge step.

Fig. 10. Change of cell thickness during cycling with lithium plating.

growth in thickness can be observed. A large part of it vanishes after reducing or turning off the charging current, but a portion of the growth may persist.

Fig. 9 shows the cell thickness behavior of one charging step in detail. Displayed is the increase in cell thickness plotted against the charge in the case of strong lithium plating. For comparison a reference curve with a low charge current of 3 A has been included. At this current, no plating had been observed in previous experiments.

At a charge current of 7 A the thickness increases faster than at the low current reference. Most likely lithium plating is the reason for this. The peak in cell thickness is reached during the constant voltage phase. At this point the amount of lithium ions which intercalate into the graphite lattice is as large as the amount of lithium which arrives at the anode through the charge current. When reducing the charge rate in constant voltage mode or after stopping the charging process the subsequent intercalation of the plated lithium becomes the dominant process. This leads to a decrease of metallic lithium at the anode and therefore to a reduction of the cell thickness.

Note that not the whole amount of plated lithium is reversible. Active lithium is lost either through an SEI building reaction with the electrolyte or through losing the contact to the active surface area forming isolated lithium metal particles or layers. This irreversible part of the lithium plating as well as the evolution of gas results in a permanent thickness increase.

Fig. 10 shows the measured thickness during cycling with severe lithium plating. The parameters were −5 °C with 7 A charge and

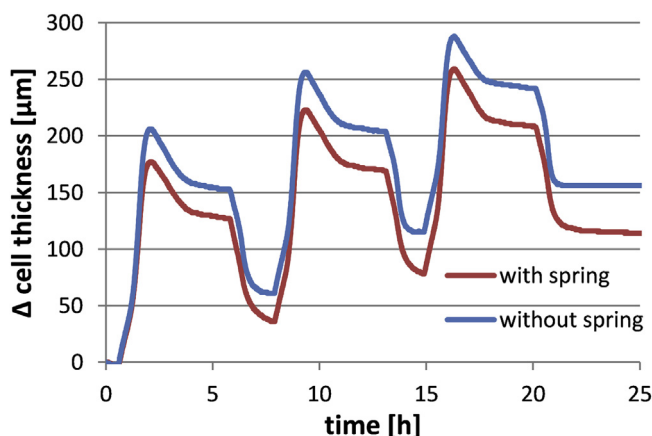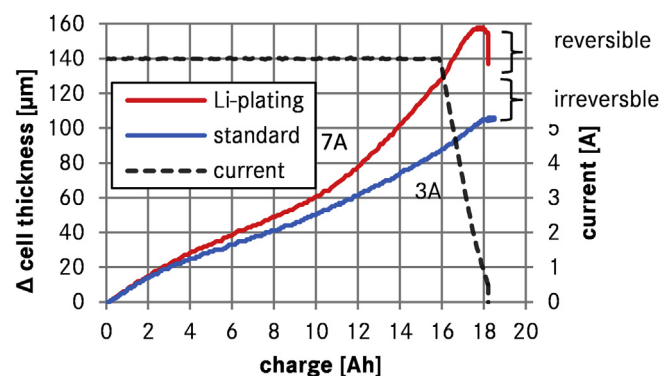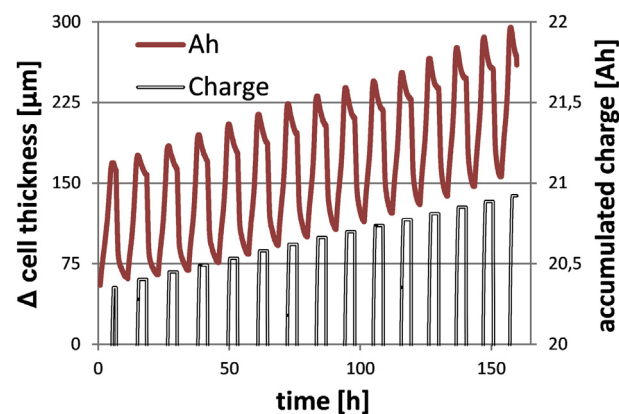Fig. 8. Recorded cell thickness in the case of strong plating.

20 A discharge current, both CCCV with a cut off current of $C/40 = 500$ mA. A relaxation time of 2 h after each charging period was provided. As the figure shows, plating leads to a residual increase of the cell thickness with a constant growing offset after every cycle.

Moreover, the accumulated capacity is constantly rising. This is because irreversibly plated lithium is lost and does not contribute to the cell voltage anymore. Therefore, to reach the same SOC or voltage level in the subsequent cycle, a higher amount of charge has to be provided which leads to the gain in the accumulated charge plot.

To prove the existence of lithium plating, the cells were disassembled after the experiments. A good correlation between the increase of thickness and the visible amount of metallic lithium on the anode was found. Monitoring the cell thickness for the detection of lithium plating is therefore an effective method for the detection of lithium plating. Especially when mapping the low temperature operation window a reduction of measurement time and effort can be achieved.

4. Conclusion

The effect of lithium plating on the volume of a Li-ion cell was investigated. A measuring setup was built for detecting changes in cell thickness with a resolution of 1 μm.

First, the change of cell thickness during standard cycling was investigated. The measurements showed that the volume change due to lithium intercalation into graphite takes place in three steps with different slopes and that it is highly reproducible. It was

shown that during standard cycling other influences like the cathode expansion, temperature or gas evolution are small.

When charging the cell with a high current causing lithium plating an additional growth could be seen. Given sufficient time, the additional growth disappears to a limited extent, which is probably due to the reversibility of lithium plating as described in the literature. However, exceeding a specific current the growth persists which indicates irreversible plating. The thickness increase is much larger than the calculated additional volume because of gas evolution or other side effects.

As a conclusion measuring the cell thickness can be an effective method for characterizing the lithium plating behavior of Li-ion pouch cells.

Acknowledgment

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